https://doi.org/10.24867/GRID-2024-p74 Original scientific paper

RECOVERY OF SILVER FROM PRINTED ELECTRONIC WASTE

Sabahattin Deniz
Marmara University, Faculty of Technology, Textile Engineering Department, Istanbul, Turkey

Abstract: *Printed electronics are preferred over traditional circuit systems in various fields such as energy, healthcare, packaging, and automotive due to reasons like lower silver ink usage, thinner product production, and suitability for mass production. The most commonly used type of ink in printed electronics is silver-based ink. Due to silver's high conductivity and the conductivity of its oxide, it is the most widely used material in printed electronic inks compared to other organic materials and metals. The growing needs of developing technology and the use of silver in other industries continually drive up its price. Considering environmental issues, the recovery of silver from printed electronics has become quite significant. This study aims to determine the effectiveness of two different methods in the recovery of silver ink printed on textile material. In the study, commercial silver paste inks were printed on textile material using screen printing. After drying, the printed samples were aged for two years, and then the silver recovery process was applied. Two methods were employed for silver recovery. In the first method, the silver-printed sample was burned at high temperature, and the silver in the resulting ash was dissolved in nitric acid. In the second method, the silver-printed sample was cut into small pieces and treated with nitric acid without burning to dissolve the silver. The amount of silver dissolved in the solution in both methods was determined using atomic absorption spectrophotometry. Additionally, the effects of nitric acid concentration on recovery were investigated. As a result, it was determined that the amount of silver recovered by the incineration method was higher, but the energy cost was also higher compared to the other method.*

Key words: silver recovery, printed electronics, sustainability, screen printing

1. INTRODUCTION

For many years, electronic circuits have been used in all devices across various aspects of our lives. In recent years, with the rapid development of smart hardware and big data, the use of printed electronics has come to the forefront, replacing traditional circuit systems. Printed electronics are rapidly growing with great potential in fields such as healthcare, energy, packaging, education, social networks, and the military. Materials such as paper, polymeric films, and textile materials are mostly used for printed electronics. The wide design options, the ability to produce thinner products, different material options, production techniques, and extensive applications have fostered increasing research interest in printed electronics. Currently, the production of conductive components generally relies on organometallic compounds, graphene, carbon nanotubes, conductive polymers, and metal nanoparticles (Islam et al., 2024). Due to their high conductivity, metal nanoparticles have become one of the most effective components (Boumeganane et al., 2022). Metals such as gold (Au), silver (Ag), and copper (Cu) are commonly used as potential conductive materials in printed electronics. Silver (Ag) is preferred for formulating conductive inks because it has the highest electrical conductivity (6.3×10^7 $S.m^{-1}$) among metals. In addition to high conductivity, it also offers advantages such as high resistance to oxidation and an applicable processing method. Therefore, silver stands out as the preferred material for printed electronics (Xia et al., 2006; Ibrahim et al., 2022).

Using textile materials as the base material in printed electronics, especially because they are soft and flexible enough to wear, combining smart electronics that interact with the environment with daily textiles has great potential, especially in improving human health, disease prevention, and healthcare services (Chen et al., 2022; Yuan et al., 2022).

The development of printed electronics essentially requires producing a conductor on a material. The process ensures that the conductor completely accumulates on the base material to be used. The processes in conventional printed circuit production can cause the use and disposal of large amounts of conductive material that is often toxic, environmentally harmful, and non-biodegradable. However, printing, that is, locally depositing the active material in ink/paste form onto textiles, can provide a sustainable solution both environmentally and economically compared to the conventional printed circuit production process. Additionally, the printing technique stands out with simple, low-cost, time-saving, versatile, and environmentally friendly production technologies on textile surfaces. Therefore, the next trend in wearable

e-textile production is rapidly moving towards printing all electronic parts onto textiles (Kastner et al., 2017).
The printing process involves the controlled deposition of material onto a substrate to produce a predefined pattern for decorative or functional purposes. Despite the presence of other deposition processes such as painting or spraying, printing becomes even more significant as it can quickly reproduce the same layers as the original. Screen printing, gravure printing, flexographic printing, continuous inkjet printing, and on-demand inkjet printing are the printing technologies used for e-textile production Hu et al., 2018). The types of printing may have advantages over each other depending on the physical and chemical properties of the material and ink to be used. However, one of the biggest advantages of screen printing is that it allows the use of a wide range of substrates, such as paper, cardboard, polymer materials, textiles, wood, metal, ceramic, glass, and leather. Screen printing is by far the most widely used method in wearable e-textile applications (Izdebska & Thomas, 2016). To date, researchers have applied screen printing for the manufacturing of textile-based strain, pressure, temperature, and humidity sensors (Filipowska et al., 2018). Various textile-based biosensors, such as electrocardiogram (ECG), electroencephalography (EEG), electromyography (EMG), and electrooculography (EOG), have also been reported to be made using the screen printing method (Gerlach et al., 2015; Jost et al., 2013). In addition, several screen-printed textile-based supercapacitors and heating elements have been demonstrated (Wu et al., 2019).
Materials that are not recycled at the end of their life cycle bring significant environmental and economic burdens due to pollution formation and the loss of valuable resources. The extensive usage of conventional or printed electronics makes the waste management of these materials after they become waste a crucial issue. Considering the rapid and increasing turnover rate of electronic products, electronic waste (e-waste) containing toxic substances and valuable metals like gold and silver is an urgent environmental, safety, and economic concern. However, recycling procedures for the recyclability of electronics can lead to secondary pollution and insufficient recovery of valuable components (Mondal et al., 2023). Regarding electronic waste, a study conducted in 2018 showed that 533 tons of silver were used in the electronics industries worldwide (Alexander et al., 2019). According to e-waste production studies, the amount of e-waste produced worldwide in 2018 was around 53.6 million tons (Forti et al., 2020). According to Statista, the amount of e-waste production in 2022 was 62 million tons. Furthermore, this trend is projected to persist, with annual e-waste production anticipated to reach 82 million metric tons by 2030 (Baldé et al., 2024). However, the total amount of e-waste collected for recycling was only about 11% (Mondal et al., 2023). These data suggest that electronic waste recycling is not adequately provided, which means both increasing negative environmental impacts and continuing negative economic effects due to the lack of recovery of valuable metals. From this perspective, the importance of studies on the recovery of electronic waste is clearly understood. As a solution to adverse environmental impacts, materials called transient electronics are produced. These are intended not to cause environmental pollution when various layers degrade after their operational lifetime. For this, embedding enzyme nanoclusters into plastics can program the degradation of polyesters under industrial composting conditions (Kwon et al., 2022). Integrating these new developments into composite materials is thought to serve sustainable printed electronics and the reduction of e-waste.
Methods such as exposure to high temperatures (Jaziri et al., 2024), ultrasound-assisted chemical flotation (Chen et al., 2023), pyrometallurgical, chemical leaching, and bioleaching (Schwartz et al., 2024) are applied for the recovery of metals from printed electronics or, in general, electronic waste.
In this study, it was aimed to determine the effectiveness of two different methods for the recovery of silver from textile material printed with silver ink. In the study, commercial silver paste inks were printed on textile material using screen printing. After drying and fixing, the printed samples were conditioned in oven at 100^{o}C for an hour and kept in desiccator then, the silver recovery process was applied. Two methods were employed for silver recovery. In the first method, the silver-printed sample underwent combustion at high temperature, and the silver in the resulting ash was dissolved in nitric acid. In the second method, the silver-printed sample was cut into small pieces and treated with nitric acid without combustion to dissolve the silver. The amount of silver dissolved in the solution in both methods was determined using atomic absorption spectrophotometry. Additionally, the effects of nitric acid concentration and time on recovery were investigated.

2. METHODS

2.1 Materials

Silver paste ink for screen printing on the fabric was obtained from Nanovatif Material Technologies Türkiye. Dyed and finished 100% cotton fabric was used for preparing e-textile material. ATAÇ GK40 RKL was used for fixing the printed textile material. Nitric acid (HNO_3) was procured from Carlo Erba. Distilled water was sourced from ISOLAB LWD-3008, and Precisa XB220 model balance was employed for mass measurements. The separation of solids from solutions after combustion was carried out using the ISOLAB 0.45 μm filter. Yellow line OS 10 basic shaker was employed for shaking. Silver analyses were performed using Analytik Jena ZEENit 700 Flame Atomic Absorption Spectrometer (FAAS). Thermal studies were performed using a Binder oven and Lenton CAL 8000 furnace.

2.2 Fabric printing

Screen printing, a method introduced in the late 9th century, is a traditional printing technique applied to a wide variety of materials, including textiles, ceramics, glass, plastics like polyethylene and polypropylene, paper, metal, and wood. It is often favoured over alternatives such as hand block printing, engraved roller printing, heat transfer, and inkjet printing due to its simplicity and low cost. In this process, a design is transferred onto a fine mesh screen, with non-printing areas blocked by an impermeable substance. Ink is then pressed through the mesh using a squeegee to print the design (Kazani et al., 2012; Ragab et al., 2022). In this study, a monofilament polyester 230 mesh with a thickness of 110 µm and a sieve opening of 45% was used. The printing design consisted of a rectangle measuring 8 x 4 cm. The printing of silver ink onto the fabric involved four print passes, meaning the squeegee was passed over the stencil four times. Then, the printed fabric was fixed at 120^oC for 15 minutes. The textile material, before and after printing, was shown in Figure 1.

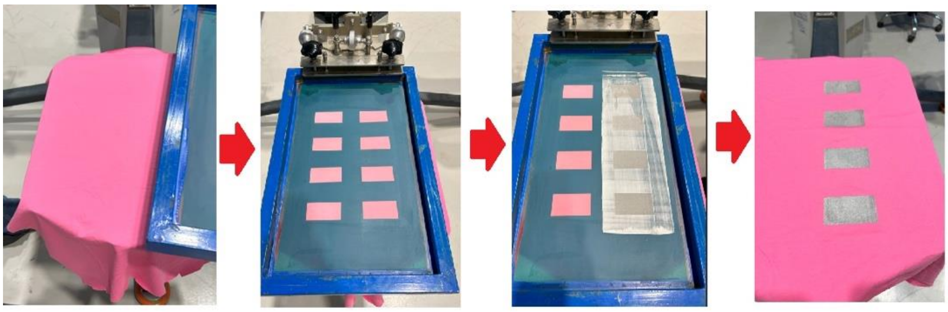

Figure 1: Screen printing on the cotton fabric

Conductivity of printed fabric was tested by a simple electric circuit using led diodes. While electrical conductivity was not observed in the fabric where silver ink printing was not applied, it was observed that the printed parts had very good electrical conductivity (Figure 2). The manufacturer informed us that the resistance of the silver ink used is 10 milliohms. Since the aim of this study is to investigate the recovery of silver from silver-printed textile materials, no studies were conducted on print quality or more detailed measurements of the electrical conductivity of the print. These topics are beyond the scope of our study.

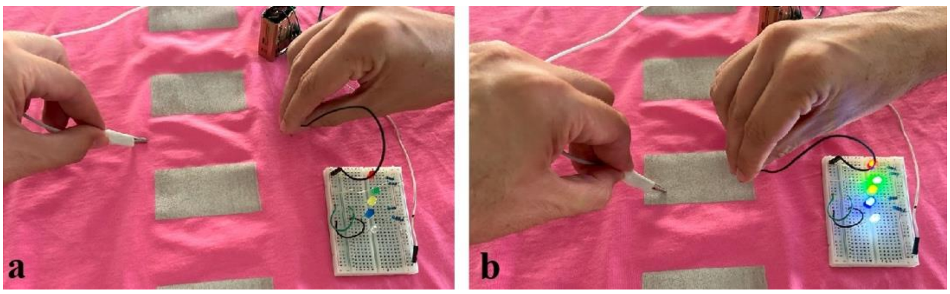

Figure 2: Conductivity of (a) unprinted cotton fabric and (b) silver printed cotton fabric

2.2 Silver recovery studies

Two different methods have been employed for recovery of silver from the printed fabric. First, silver recovery from the printed fabric was carried out using the traditional method of incineration followed by acid leaching, which is also used to analyze the metal content in fabrics (Analytical methods for a Textile Laboratory, 1984). For this, a certain amount of the printed fabric sample was burned at 550°C for different durations (Figure 3), and the remaining ash was treated with nitric acid. After the cloudy mixture was filtered through a 0.45 µm filter and filled up to a specific volume, the silver content was determined using flame atomic absorption spectrophotometry.

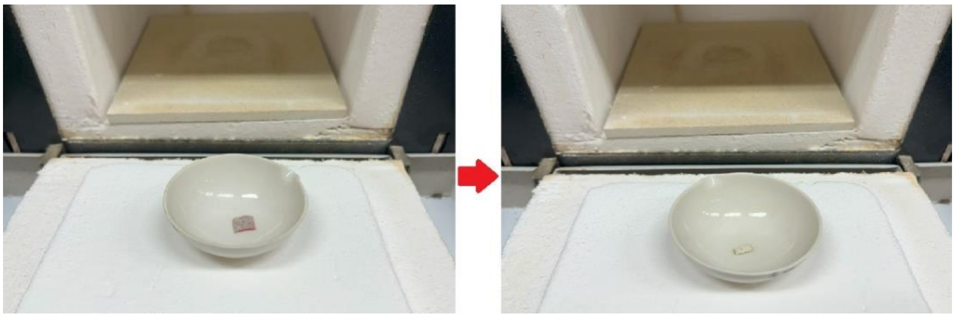

Figure 3: Incineration of printed cotton fabric

As a second method, direct leaching from the printed fabric using an oxidizing acid was attempted. For this purpose, 1 cm x 1 cm pieces of printed fabric were shaken in 20 mL of HNO_3 solutions at concentrations of 0.5, 1.0, 2.5, 5.0, and 10.0 M for different durations (Figure 4), and the amount of silver transferred into the solution was determined using flame atomic absorption spectrophotometry.

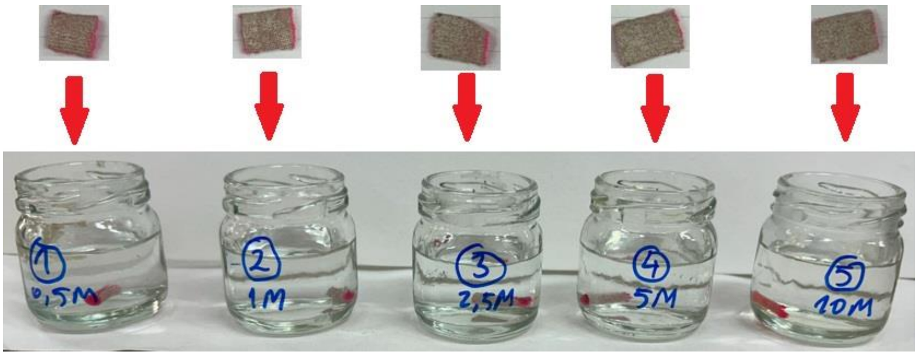

Figure 4: Direct leaching of printed cotton fabric

3. RESULTS

In this study, the efficiency comparison between the traditional incineration and acid leaching method and the direct oxidizing acid leaching method for silver recovery from silver-printed e-textiles was carried out. In the traditional incineration and acid leaching method, only the effect of incineration time on recovery was examined. In the direct oxidizing acid leaching method, the effects of acid concentration and exposure time to the acid on recovery were investigated.

3.1 Incineration time

To determine the metal content of a fabric, the 'analytical methods for a textile laboratory' published by the American Association of Textile Chemists and Colorists are mostly applied. In this method, the fabric is first incinerated at 550°C until it turns into white ash. Then, this white ash is treated with different acids depending on the type of metal to be analyzed, allowing the metal ions to be extracted from the fabric into the solution. In this study, 2, 5, 10, 15 minutes of incineration time were carried out for recovery of silver from the printed fabric. The results showed that ten minutes of incineration is sufficient for recovering all the silver from the printed fabric (Figure 5).

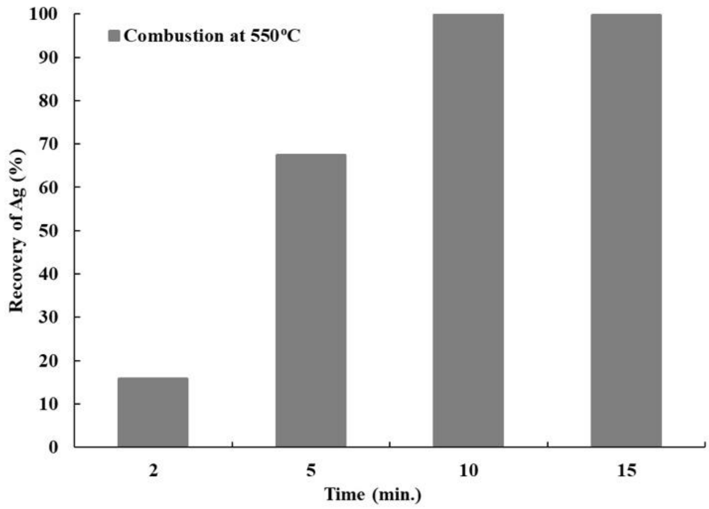

Figure 5: Effect of incineration time on recovery of silver

3.2 Concentration of HNO_3

To investigate the effect of HNO_3 concentration on the recovery of silver from the printed fabric, the fabric was treated with five different concentrations of HNO_3 solution, ranging from 0.5 M to 10.0 M. According to the obtained data, recovery of silver increases as the HNO_3 concentration increases (Figure 6).

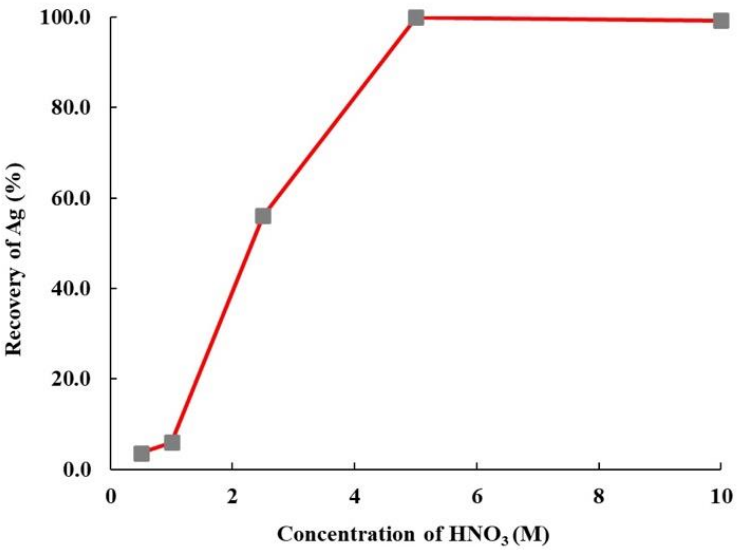

Figure 6: Effect of HNO_3 concentration on recovery of silver

3.3 Treatment time with HNO_3 solution

One of the important parameters for the recovery of silver from the printed fabric is the treatment time of the fabric with HNO_3 solution. To determine the optimum treatment time, the printed fabric was treated with different concentrations of HNO_3 solutions for varying times, ranging from 2 minutes to 4 hours. According to the obtained results, it was observed that the treatment time required to achieve maximum recovery decreased significantly as the HNO_3 concentration increased. Particularly at concentrations of 5.0 M and 10.0 M, maximum recovery values were reached within a few minutes. To better understand the obtained results, the data are presented in three different ways in Figure 7.

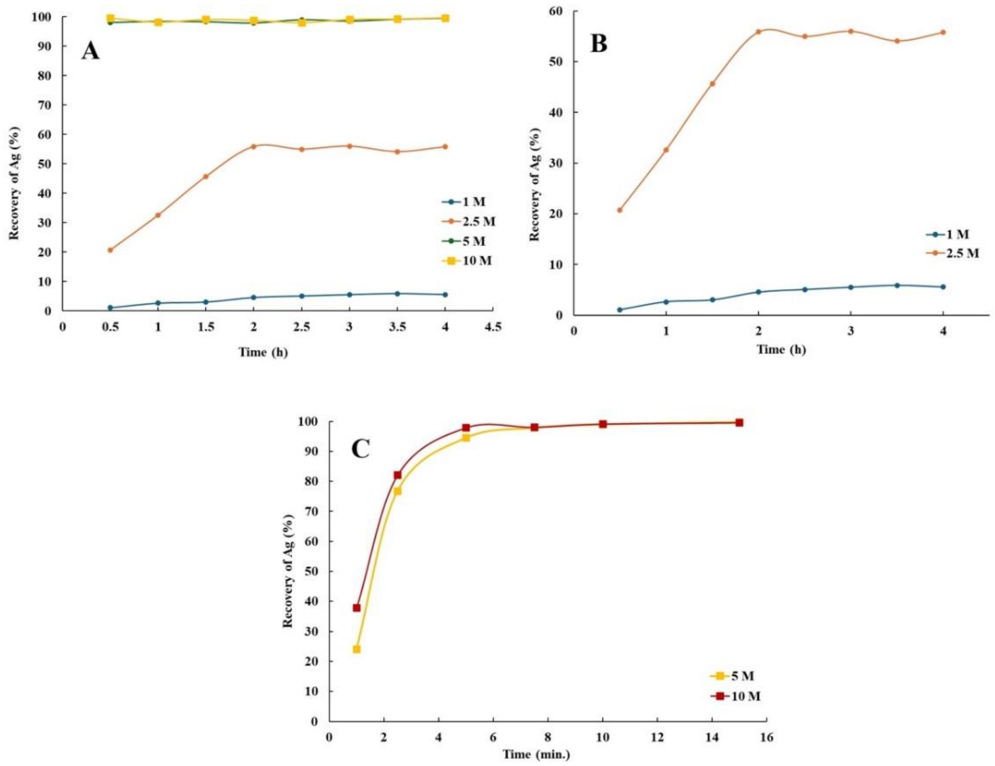

Figure 7: Effect of treatment time with (A) all HNO_3 concentrations (B) with 1.0 M and 2.5M HNO_3 and (C) with 5.0 and 10.0 M HNO_3 on recovery of silver

4. DISCUSSION

Metals in their elemental form react with acids to be oxidized into water-soluble cations. However, noble metals only react with oxidizing acids or acid mixtures. Silver metal, reacts with oxidizing acids to form the water-soluble Ag^+ ion. Therefore, nitric acid is suitable for dissolving elemental silver metal into a water-soluble form. Additionally, the nitrate anion present in nitric acid can also remain in a water-soluble form with silver ions. The chemical reaction between silver and non-concentrated nitric acid at room temperature was given in Equation (1). For this reason, nitric acid was chosen in this study to easily recover metallic silver from printed fabric.

$$3\,Ag_{(s)} + 4\,HNO_{3\,(aq)} \rightarrow 3AgNO_{3\,(aq)} + NO_{(g)} + 2H_2O_{(l)} \quad (1)$$

Additionally, silver recovery from the same printed fabrics was also attempted using the incineration and acid leaching method. As shown in Figure 5, it was observed that all the silver in the printed fabric could be recovered within a short period of 10 minutes using this method. However, this method requires a significant amount of electrical energy. Instead, the recoverability of silver metal was investigated using nitric acid, an oxidizing acid, without incineration, thereby avoiding the high energy requirement. According to the obtained results, recovery increased with the concentration of nitric acid, as seen in Figure 6. It is understood that all the silver metal in the fabric is recovered at concentrations of 5.0 M and higher. Another important parameter is the contact time with the acid solution. The dissolution of the polymeric resin, which serves as a binder in addition to the silver metal in the printing ink, is essential for the acid to eventually come into contact with the silver metal. It is thought that at concentrations of 5.0 M and higher, this resin is completely degraded, and the silver metal reacts completely with the acid to dissolve. Additionally, as the acid concentration increases, the amount of acid available to react stoichiometrically with the silver also increases, which may explain the increased recovery. The low recovery at lower concentrations might be due to the insufficient amount of H^+ ions from the acid to dissolve all the silver metal. This needs to be clarified through further studies and is also a topic for future research. In this study, it was found that 20 mL of 5.0 M HNO_3 solution was sufficient to recover all the silver from a fabric piece containing approximately 15 mg of silver, and it was observed that all the silver metal could be dissolved into the solution within a few minutes.

5. CONCLUSIONS

In this study recovery of silver from the printed cotton fabric carried out by chemical leaching using nitric acid solution and incineration and acid leaching methods. Screen printing was applied to 100% cotton fabric using an ink containing approximately 70% silver and a polyurethane resin binder. The optimum nitric acid concentration and treatment time required to recover silver from the printed fabric were determined. According to the obtained data, it was found that when a printed fabric piece containing approximately 15 mg of silver was shaken with 5.0 M HNO_3 for 5 minutes, all the silver in the fabric could be recovered.
Additionally, with the incineration and acid leaching method, it was observed that all the silver in the printed fabric could be recovered by holding the fabric at 550°C for 10 minutes, followed by treatment with 10.0 M nitric acid.
As a result, it was concluded that silver can be successfully recovered from the printed fabric using both methods. However, due to the high electrical energy consumption of the incineration method, it was concluded that the direct treatment method with nitric acid solution, applied in this study, would be more suitable due to its lower energy cost and ease of application.

6. ACKNOWLEDGMENTS

The author sincerely thanks Nanovatif Material Technologies Inc. for supplying the silver paste ink, Prof. Dr. Burcu Yılmaz and Res. Assist. Onur Atak for supplying the cotton fabric and their help in performing the screen printing, and Assoc. Prof. Dr. Emine Arman Kandırmaz for her support in the completion of this study.

7. REFERENCES

Alexander, C., Litosh, S., Wiebe, J., Yao, W., Saha, D., Norton, K., Li, S., Guy, F., Scoot-Gray, N. & Goenka, S. (2019) *World silver survey 2019*, The Silver Institute, Washington D.C. Available from: https://www.silverinstitute.org/wp-content/uploads/2019/04/WSS2019V2.pdf [Accessed 17th June 2024].

American Association of Textile Chemist and Colorists (1984) Analytical methods for a textile laboratory.

Baldé, C.P., Kuehr, R., Yamamoto, T., McDonald, R., D'Angelo, E., Althaf, S., Bel, G., Deubzer, O., Fernandez-Cubillo, E., Forti, V., Gray, V., Herat, S., Honda, S., Iattoni, G., Khetriwal, D. S., Cortemiglia, V. L., Lobuntsova, Y., Nnorom, I., Pralat, N. & Wagner, M. (2024) The global e-waste monitor, International Telecom- munication Union (ITU) and United Nations Institute for Training and Research (UNITAR). Available from: https://ewastemonitor.info/wp-content/uploads/2024/03/GEM_2024_18-03_web_page_per_page_web.pdf [Accessed 17th June 2024].

Boumeganane, A., Nadi, A., Cherkaoui, O. & Tahiri, M. (2022) Inkjet printing of silver conductive ink on textiles for wearable electronic applications. *Materials Today: Proceedings*. 58 (4), 1235-1241. Available from: doi: 10.1016/j.matpr.2022.01.469

Chen, L., He, J.Y., Zhu, L., Yao, Q., Sun, Y., Guo, C.H., Chen, H. & Yang, B. (2023) Efficient recovery of valuable metals from waste printed circuit boards via ultrasound-enhanced flotation. *Process Safety and Environmental Protection*. 169, 869-878. Available form: doi: 10.1016/j.psep.2022.11.046

Chen, G., Xiao, X., Zhao, X., Tat, T., Bick, M. & Chen, J. (2022) Electronic textiles for wearable point-of-care systems. *Chemical Reviews*. 122 (3), 3259-3291. Available from: doi: 10.1021/acs.chemrev.1c00502

Filipowska, B., Wiśniewski, B. & Zawadzka Michalak, L. (2018) Creation of electro-conductive paths and patterns by screen printing on textile bases. *Textile Research Journal*. 88, 261 - 274. Available from: doi: 10.1177/0040517516679146

Forti, V., Balde, C. P., Kuehr, R. & Bel, G. (2020) The Global E-waste Monitor 2020: Quantities, flows and the circular economy potential - UNU Collections. Available from: https://collections.unu.edu/view/UNU:7737 [Accessed 17th June 2024].

Gerlach, C., Krumm, D., Illing, M., Lange, J., Kanoun, O., Odenwald, S. & Hubler, A. (2015) Printed MWCNT-PDMS-Composite pressure sensor system for plantar pressure monitoring in ulcer prevention. *IEEE Sensors Journal*. 15, 3647-3656. Available from: doi: 10.1109/JSEN.2015.2392084

Hu, G., Kang, J., Ng, L.W., Zhu, X., Howe, R.C., Jones, C.G., Hersam, M.C. & Hasan, T. (2018) Functional inks and printing of two-dimensional materials. *Chemical Society Reviews*. 47 9, 3265-3300. Available from: doi: 10.1039/c8cs00084k

Ibrahim, N., Akindoyo, J.O. & Mariatti, M. (2022) Recent development in silver-based ink for flexible electronics. *Journal of Science: Advanced Materials and Devices*. 7 (1), 100395. Available from: doi: 10.1016/j.jsamd.2021.09.002

Islam, M.R., Afroj, S., Yin, J., Novoselov, K.S., Chen, J. & Karim, N. (2024) Advances in printed electronic textiles. *Advanced Science*. 11, 2304140. Available from: doi: 10.1002/advs.202304140

Izdebska, J., Thomas, S. (editors) (2016), *Printing on polymers fundamentals and applications*, Plastic Design Library, USA, Elsevier.

Jaziri, N., Schulz, A., Bartsch, H., Müller, J. & Tounsi, F. (2024) A novel 2-in-1 heat management and recovery system for sustainable electronics. *Energy Conversion and Management*. 303, 118171. Available from: doi: 10.1016/j.enconman.2024.118171

Jost, K., Stenger, D., Perez, C., McDonough, J., Lian, K., Gogotsi, Y. & Dion, G. (2013) Knitted and screen printed carbon-fiber supercapacitors for applications in wearable electronics. *Energy and Environmental Science*, 6, 2698-2705. Available from: doi: 10.1039/C3EE40515J

Kastner, J., Faury, T., Außerhuber, H.M., Obermüller, T., Leichtfried, H., Haslinger, M.J., Liftinger, E., Innerlohinger, J., Gnatiuk, I., Holzinger, D. & Lederer, T. (2017) Silver-based reactive ink for inkjet-printing of conductive lines on textiles. *Microelectronic Engineering* 176, 84-88. Available from: doi: 10.1016/j.mee.2017.02.004

Kazani, I., Hertleer, C., Mey, G.D., Schwarz, A., Guxho, G. & Langenhove, L.V. (2012) Electrical conductive textiles obtained by screen printing. *Fibres & Textiles in Eastern Europe*, 20, 57-63. Available from: http://www.fibtex.lodz.pl/pliki/Fibtex_(raou52b2tj04ebp0).pdf [Accessed 17th June 2024].

Kwon, J., DelRe, C., Kang, P., Hall, A., Arnold, D., Jayapurna, I., Ma, L., Michalek, M., Ritchie, R.O., & Xu, T. (2022) Conductive ink with circular life cycle for printed Eelectronics. *Advanced Materials*. 34, 2202177. Available from: doi: 10.1002/adma.202202177

Mondal, M.S., Paul, A. & Rhaman, M. (2023) Recycling of silver nanoparticles from electronic waste via green synthesis and application of AgNPs-chitosan based nanocomposite on textile material. *Scientific Reports*. 13, 13798. Available from: doi: 10.1038/s41598-023-40668-7

Ragab, M., Othman, H.A. & Hassabo, A. G. (2022) An overview of printing textile techniques. *Egyptian Journal of Chemistry*. 65 (8), 749-761. Available from: 10.21608/ejchem.2022.131477.5793

Schwartz, E., He, H., Frost, K., Nguyen, B. H., Ogunseitan, O.A. & Schoenung, J.M. (2024) Comparative life cycle assessment of copper and gold recovery from waste printed circuit boards: Pyrometallurgy, chemical leaching and bioleaching. *Journal of Hazardous Materials*. 473, 134545. Available from: doi: 10.1016/j.jhazmat.2024.134545

Wu, L., Qian, J., Peng, J., Wang, K., Liu, Z., Ma, T., Zhou, Y., Wang, G. & Ye, S. (2019) Screen-printed flexible temperature sensor based on FG/CNT/PDMS composite with constant TCR. *Journal of Materials Science: Materials in Electronics*, 30, 9593-9601. Available from: doi: 10.1007/s10854-019-01293-1

Xia, X., Xie, C., Cai, S., Yang, Z. & Yang, X. (2006) Corrosion characteristics of copper microparticles and copper nanoparticles in distilled water. *Corrosion Science*. 48 (12), 3924-3932. Available from: doi: 10.1016/j.corsci.2006.04.007

Yuan, Y., Liu, B., Li, H., Li, M., Song, Y., Wang, R., Wang, T. & Zhang, H. (2022) Flexible wearable sensors in medical monitoring. *Biosensors*, 12, 1069. Available from: doi: 10.3390/bios12121069